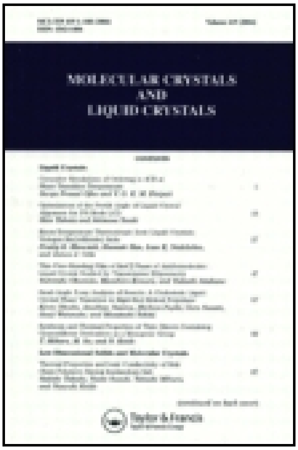

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# Hydrogen Transport through Rf-magnetron Sputtered Amorphous and Crystalline $WO_3$ Films with Hydrogen Trap Sites

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# Hydrogen Transport through Rf-magnetron Sputtered Amorphous and Crystalline $WO_3$ Films with Hydrogen Trap Sites

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The present work is aimed at investigating hydrogen transport through amorphous $WO_3$ ($a$-$WO_3$) and crystalline $WO_3$ ($c$-$WO_3$) films prepared by rf-magnetron sputtering onto indium tin oxide(ITO) glass under impermeable boundary condition in 0.1 M $H_2SO_4$ solution by using Fourier transform infra-red(FTIR) spectroscopy, cyclic voltammetry, potentiostatic current transient technique and ac-impedance technique. The FTIR spectra showed that the $a$-$WO_3$ film contained water, apart from the $c$-$WO_3$. From the results obtained form the electrochemical experiments, it was suggested that the different behaviours in cyclic voltammograms between $a$- and $c$-$WO_3$ films result from an open-structured nature of $a$-$WO_3$ film containing $H_2O$, which does not exist in the $c$-$WO_3$ film and there are three kinds of hydrogen injection sites in the films, i.e., reversibly active site, shallow trap site(reversible trap site) and deep trap site(irreversible trap site). The Mott-Schottky approach permitted us to semi-quantitatively determine the amount of the deep trap site.

Keywords: hydrogen transport; impermeable boundary condition; potentiostatic current transient; shallow trap; deep trap

## INTRODUCTION

Electrochromism is defined as a reversible colour change in a material caused by an applied potential or current[1,2]. Tungsten trioxide ($WO_3$) has been widely studied as an electrochromic material because it turns dark blue upon electrochemical reduction and transparent upon electrochemical oxidation[3-5].

It has been reported[6] that the mobility of a hydrogen ion in hydrous $WO_3$ film is expected to be higher than that in anhydrous $WO_3$ film since a hydrogen ion may move as $H_3O^+$ ion.

The roles of trap site in hydrogen transport through nickel hydroxide[7] and palladium films[8] were theoretically studied. They[7,8] concluded that the trap sites in the film have significant effect on hydrogen transport through the film. Owing to such an important effect of trap site on hydrogen transport through device using electrochromc property, it is necessary to elucidate the existence of trap site and the effect of trap site on hydrogen transport through the $WO_3$ film.

This work considers hydrogen transport through amorphous $WO_3$ (*a*-$WO_3$) and crystalline $WO_3$ (*c*-$WO_3$) films rf-magnetron sputtered onto indium tin oxide(ITO) glass in the presence of hydrogen trap sites under the impermeable boundary condition in 0.1 M $H_2SO_4$ solution by using cyclic voltammetry, potentiostatic current transient technique and ac-impedance technique.

## EXPERIMENTAL

The $WO_3$ film prepared by rf-magnetron sputtering under an appropriate condition was characterised using alpha-step stylus and X-ray diffractometry. which was detailed in a previous publication[9].

In order to identify chemical bonding in the $WO_3$ films, Fourier transform infra-red(FTIR) absorption spectra were measured on the *a*- and *c*-$WO_3$ films with the help of the attenuated total reflectance(ATR) method.

A platinum wire and a saturated calomel electrode were used as a counter electrode and a reference electrode, respectively. The 0.1 M $H_2SO_4$ solution used as electrolyte was deaerated previously for 24 h and during all electrochemical measurements by bubbling with purified nitrogen.

Cyclic voltammetry was performed on the $WO_3$ film/ITO glass specimen in 0.1 M $H_2SO_4$ solution in the potential range of -0.8 to 0.4 V(SCE) with a scan rate of 20 mV/s. Cyclic voltammetry for the *a*-$WO_3$ film was conducted to 20 redox(injection/extraction) cycles.

The $WO_3$ electrode specimen was first pre-polarized at a cathodic potential of -0.8 to -0.3 V(SCE) for constant time of $3\text{x}10^3$ s, followed by suddenly jumping the cathodic potential to 0.3 V(SCE). From this moment, resulting potentiostatic current decay transients were recorded.

The electrochemical impedance was measured by superimposing a single sinusoidal potential wave of 10 mV peak-to-peak on an applied anodic potential of 0.3 to 0.8 V(SCE) over the frequency range of 1 to $10^4$ Hz for virgin(hydrogen-uncharged) film and hydrogen trapped film. The trapped film specimen was prepared by hydrogen-charging at a cathodic potential of -0.3 V(SCE) for constant time of 200 s, followed by potential jumping to an anodic potential of 0.8 V(SCE). The cathodic and anodic potentials were successively applied to the virgin film in order to inject the hydrogen into the film and to extract the injected hydrogen from the film, respectively. Hereafter, the number of occupied irreversible trap site was semi-quantitatively determined from the difference in the donor concentration between the virgin film and the trapped film. The donor concentration in the film was calculated from the well-established Mott-Schottky relation[10,11].

## RESULTS AND DISCUSSION

Fig. 1 presents FTIR spectra of the *a*-WO$_3$ film and the *c*-WO$_3$ film. For the *a*-WO$_3$ film, a peak appeared near 3500 cm$^{-1}$ indicating that the *a*-WO$_3$ film contains water. Vangrunderbeek et al.[12] have reported that preparation of a water-free WO$_3$ film by thermal evaporation of a WO$_3$ powder or sputtering from a WO$_3$ target is impossible unless the source material is pre-baked in situ since WO$_3$ powder contains a great deal of water. On the other hand, *c*-WO$_3$ film contains no water as presented in Fig. 1. As mentioned, the water in the film enhances the movement of hydrogen ion[6]. It is probably conceivable that water makes the film structure open and hence provides a wider path for movement of hydrogen ion.

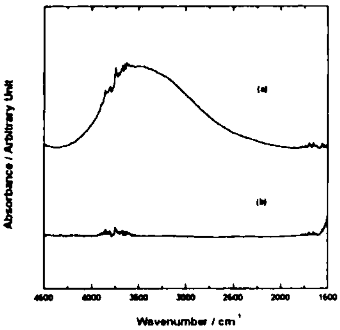


FIGURE 1 Fourier transform infra-red absorption spectra of the (a) amorphous WO$_3$ and (b) crystalline WO$_3$ films.

The cyclic voltammograms of the *a*- and *c*-WO$_3$ films are shown in Figs. 2(a) and 2(b), respectively. As presented in Fig. 2(a), cathodic current increased abruptly at about -0.7 V(SCE) and a broad anodic current peak occurred in the applied potential range of about -0.6 to -0.2 V(SCE). The abrupt increase in cathodic current is concerned with the evolution of hydrogen on and the hydrogen injection into the *a*-WO$_3$ film. The broad anodic current peak is due to the oxidation of hydrogen injected into the oxide film. It is worthwhile to note that the anodic current peak was shifted to more anodic potential as the number of cycle increased. It is probably conceivable that the injecting hydrogen is positioned first at reversibly active site for a moment and then is located at reversible trap site to bind hydrogen rather strongly than reversibly active site. As the number of cycle increases, the amount of hydrogen positioned at reversible trap site increases and the role of reversible trap site in the hydrogen injection into the $WO_3$ film is more significant so that anodic current peak shifts in the anodic direction.

From Fig. 2(b), a cathodic current which is concerned with the evolution of hydrogen on and the hydrogen injection into the *c*-$WO_3$ film increased abruptly at about -0.8 V(SCE) and a relatively sharp anodic current peak resulting from the oxidation of hydrogen injected into the oxide film was encountered at about 0 V(SCE). No anodic current peak was observed except for the oxidation current peak of hydrogen injected into the films. The separation between peak potentials at the current peaks associated with hydrogen injection and extraction is smaller for the *a*-$WO_3$ film as compared to the *c*-$WO_3$ film, indicating that the hydrogen injection and extraction kinetically run more reversibly into and from the *a*-$WO_3$ film.

The amount of the charge associated with the anodic reaction from cyclic voltammogram of the *a*-$WO_3$ film was larger than that of the *c*-$WO_3$ film. This means that the amount of hydrogen injected into the *a*-$WO_3$ film is larger than that amount into the *c*-$WO_3$ film. From the results of cyclic voltammograms, it is indicated that the hydrogen injection and extraction proceed more facilely into and from the water-containing open-structured *a*-$WO_3$ film than the water-free *c*-$WO_3$ film.

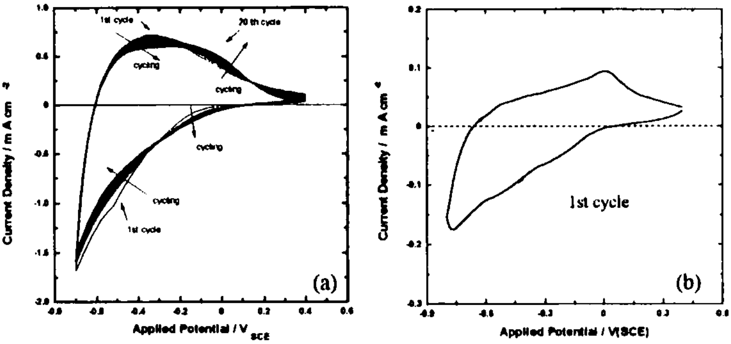
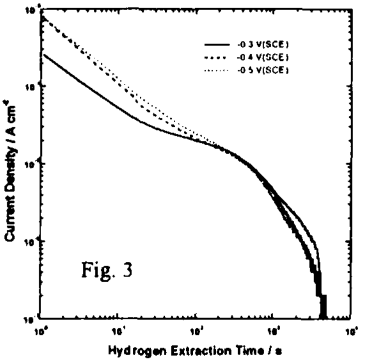


FIGURE 2 Cyclic voltammograms of the (a) amorphous $WO_3$ and (b) crystalline $WO_3$ films in 0.1 M $H_2SO_4$ solution with a scan rate of 20 mV/s. Successive cyclic voltammetry for the amorphous $WO_3$ film was conducted to 20 cycles.

Fig. 3 presents potentiostatic current decay transients obtained for the *a*-$WO_3$ film during the hydrogen extraction. The current decay transients of Fig. 3, showed two-staged variation. In the first stage, the slopes of log (current density)-log (time) plots were about -3/4. When the applied cathodic potential is jumped to an anodic potential, the space charge layer of hydrogen ion is generated because the mobility of electron is much larger than that of hydrogen ion. Faughnan et al.[13] have reported that field-driven space-charge-limited current by transport of hydrogen ion decays as $t^{-3/4}$ during the extraction of hydrogen ion assuming that significant trap sites for hydrogen ion do not exist. In the second stage, the slopes of current decay transients were lower than those of the first stage. It is expected that the deviation from the slope of -3/4 is due to the existence of reversible trap sites for hydrogen ion with relatively strong binding energy. This result is supplemented by the anodic peak shift in the successive cyclic voltammograms for the *a*-$WO_3$ film.



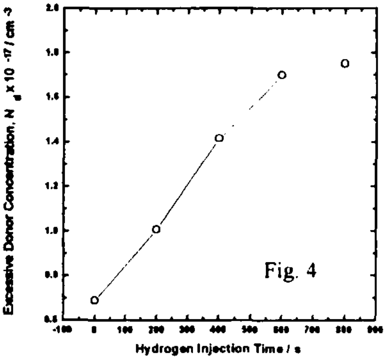


FIGURE 3 Potentiostatic current decay transients obtained from the amorphous $WO_3$ film in 0.1 M $H_2SO_4$ solution from the moment when the applied cathodic potential of -0.5 to -0.3 V(SCE) is jumped to an anodic potential of 0.3 V(SCE). The various applied cathodic potentials are indicated in the figure.

FIGURE 4 Plot of donor concentration(concentration of deep trap site) against hydrogen injection time at measuring frequency of 200 Hz.

Lampert[11] has proposed that grain boundary plays a role of deep donor Considering that the broken bond(non-bridging oxygen ion) exists along the grain boundary, it is expected that the hydrogen ion forms rather strong bond with the non-bridging oxygen ion. It seems that the hydrogen ion bound to non-bridging oxygen ion is less mobile than those bound to lattice oxygen ions interacting with tungsten ions and moreover those bound to hydroxide ion or water. Therefore the reversible trap sites of hydrogen ion may originate from the grain boundaries. '

Using the well-known Mott-Schottky relation[10,11], the uniform donor concentrations in the virgin film and the trapped film could be determined. Fig. 4 demonstrates excessive donor concentration($N_d$ (trapped film) - $N_d$ (virgin film)) in the *a*-$WO_3$ film as a function of hydrogen injection time at measuring frequency of 200 Hz. The excessive donor concentration can be regarded as the concentration of occupied deep trap sites(irreversible trap sites) since the donor concentration in the trapped film was measured after sufficient hydrogen extraction at an anodic potential of 0.8 V(SCE). The concentration of occupied deep trap sites increased with increasing injection time indicating that the quantity of hydrogen positioned at deep trap sites increased. However, the average increase rate of the concentration of occupied deep trap sites decreased with increasing injection time. It means that the amount of hydrogen trapped at the deep trap sites almost attained a saturation value, which represents the quantity of irreversible trap sites.

## CONCLUSIONS

1. From the results of cyclic voltammograms, it is indicated that the hydrogen injection and extraction proceed more facilely into and from the water-containing open-structured *a*-$WO_3$ film than the water-free *c*-$WO_3$ film.
2. The experimental results allowed one to distinguish among three kinds of hydrogen injection sites, i.e., reversibly active site, shallow trap site and deep trap site existing in the rf-magnetron sputtered amorphous $WO_3$ film.
3. The way how to semi-quantitatively determine the amount of the deep trap site was proposed on the basis of the Mott-Schottky relation.

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